

REMARKS

Claims 1-23 were pending in the application prior to this amendment. By this amendment, no claims have been cancelled, while claims 24-38 have been added in order for applicants to more fully claim what they regard as their invention. Accordingly, Applicants present claims 1-38 to the Examiner for consideration.

I. INTRODUCTION

Applicants have invented novel sheets and films formed from biodegradable thermoplastic compositions. In one embodiment of the invention, the biodegradable thermoplastic composition forming the sheet or film may include at least one type of particulate filler in order to impart certain desired properties. In one sub-embodiment, the filler particles may impart increased dead-fold to the sheet or film so that, when the sheet or film is bent, folded or otherwise deformed into a desired orientation, it will tend to maintain that orientation. In another sub-embodiment, the filler particles may aid or result in the formation of cavitation comprising tiny cavities in the vicinity of the filler particles within the sheet or film.

In an alternative embodiment of the invention, increased dead-fold may be obtained by texturing the sheet or film in order to disrupt its surface.

In one embodiment of the invention, the biodegradable thermoplastic polymer consists essentially of a synthetic polymer.

The foregoing properties, both singly and cumulatively, yield films and sheets that may advantageously be used as sandwich or other foods wraps that are able to take the place of paper or other conventional materials. Because the sheets and films are formed from biodegradable compositions, they will not persist in the environment for nearly as long as films and sheets

made from non-biodegradable materials (e.g., polyethylene, polypropylene, polyvinyl chloride and the like).

II. AMENDMENT OF THE WRITTEN DESCRIPTION

Applicants have amended the written description to correct obvious typographical errors. The written description, as originally filed, erroneously listed the glass transition temperature (Tg) of Bionelle 1001 (a polybutylene succinate polymer that is reacted with hexamethylene diisocyanate) as 30° C. Upon reviewing this value with one of the inventors, it was discovered that the Tg of Bionelle 1001 is actually -30° C. This is evident from the fact that Bionelle 1000 is listed as an exemplary "soft" biodegradable polymer. A polymer having a Tg of 30° C. would be a "stiff" polymer within the meaning of this term as defined in the specification. Thus, one of ordinary skill, when reading the specification as a whole, would logically deduce that "30° C." is a typographical error, perhaps caused by inadvertently omitting the negative sign (-), and that the correct Tg is really -30° C. That 30° C. is not the correct Tg for Bionelle 1001 is evident from page 6 of a publicly available document, the relevant portion of which is attached hereto as Exhibit A. Accordingly, no new matter is being added by this amendment to the written description.

The foregoing paragraph was also amended to provide proper subject/verb agreement.

III. REJECTION UNDER 35 U.S.C. § 112, SECOND PARAGRAPH

The Office Action rejects claim 14 under 35 U.S.C. § 112, second paragraph, as being indefinite, particularly with respect to the term "substantially free". Although Applicants believe that the term "substantially free" means that the thermoplastic starch includes only an

insubstantial quantity of plasticizer. Applicants have amended claim 14 to remove the term "substantially" and to instead recite thermoplastic starch "that consists essentially of thermoplastic starch that is free of plasticizers." In this way, Applicants have simply restated what was already inherent in claim 14 as originally presented.

Applicants point out that this amendment was not made to distinguish over the prior art. Nor was it made for lack of written description support for the term "substantially free". Applicants believe that amended claim 14 as amended should be understood to permit the inclusion of insubstantial quantities of a plasticizer such as glycerin, sorbitol, propylene glycol or water within the thermoplastic starch. Therefore, Applicants do not intend to surrender any claim scope or range of equivalents that would have otherwise pertained to claim 14.

IV. PRIOR ART REJECTION

The Office Action rejects claims 1-23 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 6,168,857 to Andersen et al. The Office Action also rejects claims 1-23 under 35 U.S.C. § 103 as being obvious over Andersen et al. Even though Applicants believe there are many features described in the claims that distinguish over Andersen et al., Applicants have amended the independent claims in order to further distinguish over this reference. We will now explain why the claims are believed to be patentable.

A. Claim 1

Claim 1 has been amended to claim an article of manufacture "wherein the sheet or film is stretched during processing so as to result in cavitation comprising tiny cavities in the vicinity of the filler particles". Support for this limitation is found at page 12, ll. 9-22 of the

specification. Andersen et al. neither teaches nor suggests stretching a sheet or film comprising a biodegradable thermoplastic composition during processing so as to result in cavitation comprising tiny cavities in the vicinity of the filler particles. Nor does Andersen et al. teach or suggest stretching a sheet or film during processing for any reason, let alone to yield the result recited in amended claim 1. Nor do the sheets or films of Andersen et al. inherently have "cavitated" as defined in amended claim 1. In view of the foregoing, Applicants believe that claim 1 is patentable over Andersen et al., either alone or in combination with any other prior art of record.

B. Claims 2-15

Claims 2-15 depend from claim 1 and are therefore patentable for the same reasons given above with respect to claim 1. Moreover, these claims may include additional allocations that serve to further distinguish over the prior art of record. For example, claim 13 requires the biodegradable thermoplastic composition to include "at least one stiff thermoplastic biodegradable polymer and at least one soft thermoplastic biodegradable polymer." Andersen et al. neither teaches nor suggests the specific polymer blend recited in claim 13.

C. Claim 16

Claim 16 has been amended to recite that the biodegradable thermoplastic composition "comprises at least one hydrophobic thermoplastic biodegradable polymer". In addition, claim 16 has been amended to recite that "the sheet or film is water-resistant". Support for these limitations is found at p. 18, l. 15 and p. 31, l. 6. Andersen et al. neither teaches nor suggests the manufacture of sheets or films that are "water-resistant" and "formed from a biodegradable

thermoplastic composition that comprises at least one hydrophobic thermoplastic biodegradable polymer". The organic polymer binders disclosed in Andersen et al. are hydrophilic polymers that are water-dissolvable or water-dispersible, namely starch and one or more auxiliary polymers. Col. 14, l. 41 – col. 19, l. 67. Because starch is a carbohydrate it is inherently hydrophilic. The auxiliary polymers are also described as being water-dissolvable or water-dispersible. Examples include cellulosic ethers, other polysaccharide materials, protein-based binders, and water-dispersible synthetic organic polymers, all of which are inherently hydrophilic. Indeed, Andersen et al. teaches that "water is added to the moldable mixture in order to dissolve, or at least disperse, the auxiliary polymer within the mixture". Because the sheets and films manufactured according to Andersen et al. comprise hydrophilic polymers they are not inherently "water-resistant". For this reason the sheets or films according to Andersen et al. may be coated or laminated with other sheets in order to improve their resistance to moisture.

In view of the foregoing, Applicants believe that amended claim 16 is patentable over Andersen et al., either alone or in combination with any other prior art of record.

D. Claim 17

Claim 17 depends from claim 16 and is patentable for at least those reasons set forth above with respect to claim 16.

E. Claim 18

Claim 18 has been amended to recite that the biodegradable thermoplastic composition "comprises at least one hydrophobic thermoplastic biodegradable polymer" and that the sheet or film is "water-resistant". For at least those reasons set forth above with respect to claim 16,

claim 18 is believed to be patentable over Andersen et al., either alone or in combination with any other prior art of record.

F. Claims 19-23

Claims 19-23 depend from claim 18 and are therefore patentable for at least those reasons set forth above with respect to claim 18.

V. NEW CLAIMS 24-38

New claims 24-38 have been added in order for Applicants to more fully claim what they regard as their invention. Support for the new claims are set forth as follows:

<u>Claim</u>	<u>Support</u>
24	Page 13, ll. 2-5
25	Page 13, ll. 5-7; original claim 1
26	Page 19, l. 19 – p. 31, l. 21 (providing several examples of stiff and soft synthetic polymers)
27	Page 7, l. 6; p. 13, l. 18; p. 16, l. 18; p. 19, l. 7; p. 19, l. 22; p. 25, l. 9; p. 25, l. 8; p. 50, l. 1
28	[same as claim 27]
29	[same as claim 26]
30	[same as claim 26]
31	Page 13, ll. 2-5
32	[same as claim 31]

- 33 [same as amended claim 1]
- 34 Original claim 1
- 35 [same as claim 26]
- 36 Page 19, l. 19 – p. 31, l. 21 (providing several examples of synthetic polymers)
- 37 [same as claim 26]
- 38 Original claim 8

New dependent claims 24-31, 33-35 and 37-38 are patentable at least because the claims from which they depend are patentable. In addition, these claims may include additional limitations that further distinguish over the prior art of record.

New independent claim 32 is patentable because Andersen et al. neither teaches nor suggests the manufacture of a film or sheet in which "at least a portion of the filler particles protrude from a surface of the sheet or film". Moreover, the sheets or films according to Andersen et al. would inherently not have filler particles that protrude from the sheet surface in view of how the sheets are formed (*i.e.*, between metal rollers). The smooth rollers of Andersen et al. yield sheets having a relative uniform surface.

New claim 36 is patentable because Andersen et al. neither teaches nor suggests the manufacture of a film or sheet from a "a biodegradable thermoplastic composition that consists essentially of at least one synthetic thermoplastic biodegradable polymer". The term "synthetic polymer" describes a class of polymers that exclude "natural polymers" (*i.e.*, starch, cellulose, other polysaccharides, and proteins). In contrast to claim 36, Andersen et al. discloses "starch-bound" sheets and films that necessarily include a substantial quantity of starch, a natural, in

order to have certain properties. *E.g.*, col. 5, ll. 40-44; col. 13, ll. 9-12 (starch is described as "essential"); col. 15, ll. 15-18 (sheets get strength by gelatinizing the starch binder and then evaporating water away); col. 16, ll. 25-29.

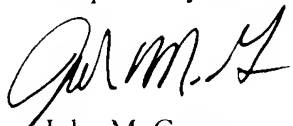
VI. CONCLUSION

In view of the foregoing, Applicants believe the claims as now presented are in allowable form. In the event that the Examiner finds any remaining impediment to the prompt allowance of this application, which could be clarified by a telephonic interview, or which is susceptible to being overcome by means of an Examiner's Amendment, the Examiner is respectfully requested to initiate the same with the undersigned attorney.

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE".

Dated this 5th day of February 2003.

Respectfully submitted,



John M. Gynn
Attorney for Applicants
Registration No. 36,153

WORKMAN, NYDEGGER & SEELEY
1000 Eagle Gate Tower
60 East South Temple
Salt Lake City, Utah 84111
Telephone: (801) 533-9800
Facsimile: (801) 328-1707

JMG:cm

W: 11527 355 CM0000002429V001.doc

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

The paragraph beginning at page 29, line 9 has been amended as follows:

Another class of "soft" aliphatic polyesters are based on repeating succinate units such as polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and polyethylene succinate (PES). Each of these succinate-based aliphatic polyesters [are] is manufactured by Showa High Polymer, Ltd. and [are] sold under the trade name BIONELLE. PBS (Bionolle 1001) has a glass transition temperature of -30° C and a melting point of 114° C. PBSA (Bionolle 3001) has a glass transition temperature of -35° C and a melting point of 95° C. PES (Bionolle 6000) has a glass transition temperature of -4° C and a melting point of 102° C.

IN THE CLAIMS:

Claims 1, 14, 16 and 18 have been amended as follows:

1. (Amended) An article of manufacture comprising a sheet or film formed from a biodegradable thermoplastic composition that includes at least one thermoplastic biodegradable polymer and at least one type of filler particles, [at least a portion of the filler particles having particle size diameters that are equal to or greater than the thickness of] wherein the sheet or film is stretched during processing so as to result in cavitation comprising tiny cavities in the vicinity of the filler particles.

14. (Amended) An article of manufacture as defined in claim 13, wherein at least a portion of the soft thermoplastic biodegradable polymer comprises thermoplastic starch that [is] consists essentially of thermoplastic starch that is [substantially] free of plasticizers.

16. (Amended) An article of manufacture consisting essentially of a sheet or film formed from a biodegradable thermoplastic composition that comprises at least one hydrophobic thermoplastic biodegradable polymer, wherein the sheet or film is water-resistant and has been textured so as to have dead-fold of at least about 70%.

18. (Amended) An article of manufacture comprising a sheet or film formed from a biodegradable thermoplastic composition that comprises at least one hydrophobic thermoplastic biodegradable polymer and at least one type of filler particles included in an amount so that the sheet or film has dead-fold of at least about 70%, wherein the sheet or film is water-resistant.

NEW BIODEGRADABLE POLYMERS
FROM RENEWABLE RESOURCES

YAN LIU



Department of Polymer Technology
Royal Institute of Technology
Stockholm, Sweden
2000

New Biodegradable Polymers from Renewable Resources

YAN LIU

*Department of Polymer Technology, Royal Institute of Technology (KTH),
S-10044 Stockholm, Sweden*

Abstract

High molecular weight poly(ester-carbonate)s have been prepared by a two-step chain-extension reaction performed on oligomeric α,ω -bishydroxyl-terminated poly(1,3-propylene succinate). α,ω -Bishydroxyl-terminated copolymeric oligomers of 1,3-propylene succinate/1,4-cyclohexanedimethylene succinate were obtained by thermal polycondensation of 1,3-propanediol/1,4-cyclohexanedimethanol/succinic acid mixtures having different composition, and subsequently chain extended using phosgene as coupling agent, which leads to aliphatic/alicyclic copoly(ester-carbonate)s. New high molecular weight amphiphilic block copolymers of poly(ester-ether-carbonate), containing poly(1,3-propylene succinate) and poly(ethylene glycol) (PEG) segments in their main chain, were synthesized by a two-step chain-extension reaction performed on a thermally-polycondensed α,ω -bishydroxyl-terminated oligomeric poly(1,3-propylene succinate) with PEG1000 and PEG2000, respectively. The new polymers, besides having a biodegradable backbone, derive from two monomers, 1,3-propanediol and succinic acid respectively, which can be obtained from renewable resources. Therefore, they have a potential as environmental friendly materials.

The molecular characterization by $^1\text{H-NMR}$ and IR spectroscopy, the molecular weight and molecular weight distribution by SEC and the main thermal properties by DSC of all synthesized materials are reported. Spectroscopic characterizations were in full agreement with the proposed structures. Thermal characterization demonstrated that an increase in the cyclic ester unit content leads to an increase in T_m and T_g of the copolymers. Solubility tests indicated that the introduction of hydrophilic PEG segments into the high molecular weight polysuccinate imparts apparent amphiphilic character to the new materials. This is expected to influence even their biocompatibility and biodegradability.

The properties of aliphatic homopolyesters from renewable monomers, 1,3-propanediol and succinic acid, were improved by introducing aromatic urethane into the main chain of polymers, which gives place to the formation of strong hydrogen bonds among the macromolecular chains of the material. Segmented polyester-urethanes (PEU) were synthesized from di-hydroxyl-terminated poly(trimethylene succinate), chain extended with 4,4'-diisophenylmethane diisocyanate (MDI). The materials were characterized using SEC, DSC, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and INSTRON. The maximum weight average molecular weight approached 7.5×10^4 . DSC detected the T_g of the soft segment from -10 to -19°C and the T_m of the hard segment from 175 to 210°C . The average repeat number of hard segment ranges from 4.0 to 8.1 , and the average repeat number of A_nB_m unit from 3.3 to 6.4 . The average length of the hard segment decreases with increasing concentration of polyester in feeding.

The results clearly show that within the studied series the increase in soft segment content reduced both crystallinity and melting temperature of hard segment microcrystalline phase, which is accompanied by decrease in modulus due to weaker interaction among polymer chains in microcrystalline phase. The degree of crystallinity, T_g , T_m , tensile strength, elongation, and Young's modulus were influenced by the ratio between hard and soft segment as well as the molecular weight of the polyester-urethane. The introduction of the polyurethane segments significantly reduces the degradability of corresponding aliphatic polyester, although there is still enzymatic attack detectable during the enzymatic degradation. All samples exhibited significant weight losses after two months of compost simulation incubation. The higher soft-segment contents resulted in higher degradability. We concluded that the segmented polyester-urethane from 1,3-propanediol and succinic acid is a promising, processable, soluble, and biodegradable thermoplastic elastomer.

Keywords: polycondensation, block copolymer, chain extension, isocyanate, phosgene, dichloroformate characterization, biodegradation, renewable resources, 1,3-propanediol, succinic acid, polyurethane, polyester, thermoplastic elastomer.

LIST OF PAPERS

This thesis is a summary of the following papers:

- I "New Biodegradable Polymers from Renewable Resources: High Molecular Weight Poly(ester-carbonate)s from Succinic Acid and 1,3-Propanediol", Elisabetta Ranucci, Yan Liu, Margaretha Söderqvist Lindblad, Ann-Christine Albertsson, *Macromolecular Rapid Communication* (2000), in press.
- II "New Biodegradable Polymers from Renewable Resources-II: Poly(ester-carbonate)s Based on 1,3-Propylene Succinate-co-1,4-Cyclohexanedimethylene Succinate", Yan Liu, Elisabetta Ranucci, Margaretha Söderqvist Lindblad and Ann-Christine Albertsson, *Polym. Adv. Technol.*, submitted.
- III "New Biodegradable Polymers from Renewable Resources-III: Segmented Copolyesters of Poly(1,3-propanediol succinate) and Poly(ethylene glycol)", Yan Liu, Elisabetta Ranucci, Margaretha Söderqvist Lindblad, Elisabetta Ranucci and Ann-Christine Albertsson, *J. Appl. Polym. Sci.*, submitted.
- IV "New Biodegradable Segmented Polyester-Urethane from Renewable Resources: Synthesis, Characterization", Yan Liu, manuscript.
- V "New Biodegradable Segmented Polyester-Urethane from Renewable Resources: Mechanical and Biodegradable Properties", Yan Liu, manuscript.

TABLE OF CONTENTS

1. PURPOSE OF THE STUDY	1
2. INTRODUCTION	3
2.1 Monomers from renewable resources	3
2.2 Polyesters	5
2.3 Degradation of polyesters	7
2.4. Polyurethanes	8
2.5 Degradation of polyurethanes	10
2.6 Chain extension reactions	12
3. EXPERIMENTAL	14
3.1 Materials	14
3.2 Synthesis	14
3.2.1 α,ω -Bis-hydroxyl-terminated poly(1,3-propylene succinate)s	14
3.2.2 Poly(1,3-propylene succinate-carbonate)s	15
3.2.3 α,ω -Bis-hydroxyl-terminated poly(1,3-propylene succinate-co-1,4-cyclohexanedimethylene succinate)	16
3.2.4 Chain extended poly(1,3-trimethylene succinate-co-1,4-cyclohexanedimethylene succinate-carbonate)	18
3.2.5 Poly(1,3-trimethylene succinate)-co- PEG ester-ether-carbonate	19
3.2.6 Synthesis of segmented polyesters-based urethanes	20

3.3 Film preparation	20
3.4 Characterization	21
3.4.1 Differential scanning calorimetry (DSC)	21
3.4.2 Size exclusion chromatography (SEC)	21
3.4.3 Nuclear magnetic resonance spectrometry (NMR)	21
3.4.4 Mechanical test (INSTRON)	22
3.4.5 Fourier transform infrared spectroscopy (FTIR)	22
3.4.6 Dynamic mechanical analyzer (DMA)	22
3.5 Solubility	23
3.6 Degradation	23
4. RESULTS AND DISCUSSION	24
4.1 High Molecular Weight Poly(1,3-propylene succinate-carbonate)s	24
4.1.1 Chemistry	24
4.1.2 Characterization	28
4.1.2.1 Solubility	28
4.1.2.2 Thermal properties	29
4.2 Poly(ester-carbonate)s based on 1,3-propylene succinate-co-1,4-cyclohexanedimethylene succinate	30
4.2.1 Chemistry	30
4.2.2 Characterization	34
4.2.2.1 Solubility	34
4.2.2.2 Spectroscopic characterization	35
4.2.2.3 Thermal properties	36
4.3 Segmented Copolyesters of Poly(1,3-trimethylene succinate) and Poly(ethylene glycol)	37

4.3.1 Chemistry	37
4.3.2 Characterization	40
4.3.2.1 Solubility	40
4.3.2.2 Swelling rate	41
4.3.2.3 Spectroscopic characterization	42
4.3.2.4 Thermal properties	43
4.4 Segmented Polyester-Urethanes	44
4.4.1 Synthesis	44
4.4.2 Structural characterization	45
4.4.3 Mechanical properties	51
4.4.4 Thermal properties	55
4.4.5 Degradation properties	57
4.4.5.1 Enzymatic degradation	57
4.4.5.2 Compost test	59
5. CONCLUSIONS	60
6. REFERENCES	63
7. ACKNOWLEDGEMENTS	69

1. PURPOSE OF THE STUDY

The main objective of the present work is to define a series of biodegradable polymers with different properties and industrial uses from two main monomers, 1,3-propanediol and succinic acid produced by fermentation from renewable resources. The experimental work was therefore focused on the design of novel polyester-based biodegradable materials, endowed with optimum physical and biodegradation properties for the final use, using 1,3-propanediol and succinic acid. It is well known that polyesters represent one of the most promising families of biodegradable polymers, whose potential applications cover such distant fields as packaging for industrial products, mulching for agriculture, or bioresorbable biomaterials for hard tissue replacement and controlled drug delivery systems. Their degradation pattern, leading to the production of fully nontoxic substances or the starting monomers, is the most adequate to satisfy environmental requirements.

Different synthetic strategies were developed and a wide spectrum of polyester-based materials capable of satisfying several different physical requirements and therefore different practical applications were proposed. Polyester-based materials were basically prepared following the synthetic strategies reported below:

1. The first step consisted in the production of oligomeric or copolymeric α,ω -dihydroxyl-terminated oligo-succinates, by thermal polycondensation of succinic acid with 1,3-propanediol, or a mixture of 1,3-propanediol and 1,4-cyclohexanedimethanol.
2. The second step consisted accordingly in the chain extension reaction of both homopolymeric and copolymeric oligo-succinates obtained in step one *via* the

chloroformate synthesis, affording polyester-carbonate (PEC) based materials having different compositions.

3. In the third step, hydrophobic/hydrophilic segmented copolymers between α,ω -dihydroxyl-terminated oligo(propylene succinate)s and poly(ethylene glycols) (PEG) of different molecular weights were synthesized, affording poly(ester-ether-carbonates) terpolymers.
4. The last step consisted in the chain extension reaction of oligo(propylene succinate)s obtained in step one *via* the diisocyanate synthesis, affording polyester-urethanes (PEU) based materials having different compositions.

2. INTRODUCTION

2.1 Monomers from renewable resources

Industrial biotechnology has evolved as a significant manufacturing tool for products like fuel-grade ethanol, organic acids and bulk amino acids as specialty products for food and pharmaceutical applications¹. Current development projects within the chemical industry, including lactic acid and 1,3-propanediol based polymers and plastics, indicate that new biotechnological process and products may soon approach the market place, clearly targeted at the leading petrochemical bulk outlet. The recent achievements in molecular plant genetic and transgenic crop breeding will boost agrobiotechnology, agriculture and renewable materials as compelling projects for chemistry and biotechnology. New plant-based production opens horizons to valuable feed stock, intermediates and end products.

The production of 1,3-propanediol by fermentation of glycerol was reported in 1881², but little attention was paid to this microbial route for over a century. Glycerol conversion to 1,3-propanediol can be carried out by *Clostridia* as well as *Enterobacteriaceae*³. The main intermediate of the oxidative pathway is pyruvate, the further utilization of which produces CO₂, H₂, acetate, butyrate, ethanol, butanol and 2,3-butanediol. In addition, lactate and succinate are generated. In the past decade, research to produce 1,3-propanediol microbially was considerably expanded as the diol can be used for various polycondensates. In particular, polyesters with useful properties can be manufactured. A prerequisite for making a "green" polyester is a more cost-effective production of 1,3-propanediol, which, in practical terms, can be

only achieved by using an alternative substrate, such as glucose instead of glycerol⁴. Estimation of product costs for a 10,000 t/a plant indicates that the microbial process can become more attractive than the chemical route.

Succinic acid, derived from fermentation of agricultural carbohydrates, has a specialty chemical market in industries producing food and pharmaceutical products, surfactants and detergents, green solvents and biodegradable plastics, and ingredients to stimulate animal and plant growth. As a carbon-intermediate chemical, fermentation-derived succinate has the potential to supply over 2.7×10^8 kg industrial products/year including: 1,4-butanediol, tetrahydrofuran, γ -butyrolactone, adipic acid, n-methylpyrrolidone and linear aliphatic esters. Succinate yields as high as 110 g/l have been achieved from glucose by the newly discovered rumen organism *Actinobacillus succinogenes*^{5,6}. Succinate fermentation is a novel process because the greenhouse gas CO₂ is fixed into succinate during glucose fermentation. Succinic acid can be produced by *Anaerobiospirillum succiniciproducens*, using glucose, but even lactose, sucrose, maltose and fructose as carbon sources.

New developments in end-product recovery technology, including water-splitting electrodialysis and liquid/liquid extraction have lowered the cost of succinic acid production to U.S. \$ 0.55/kg at the 75 000 tonne/year level and to \$ 2.20/kg at the 5000 tonne/year level⁷.

2.2. Polyesters

Polyesters are heterochain macromolecular substances characterized by the presence of carboxylate ester groups in the repeating units of their main chain. The traditional procedure for preparing linear aliphatic polyesters consists in the thermal polycondensation of diacids with diols, or in the self-condensation of hydroxyacids, followed by the elimination of water. Aliphatic polyesters have been known for a long time and were investigated as part of Carothers pioneering studies of polymerization around the 1930s⁸. Full understanding of the polymerization kinetic, based on consideration on low molecular weight analogues is ascribable to Flory⁹.

Polyesters represent a significant family of degradable materials, whose degradation products, the starting diol and acid, or hydroxyacid can enter the metabolic cycles of bioorganisms. For this reason they can be defined as potentially environmental friendly materials¹⁰.

Through variation in molecular architecture and modulation by copolymerization, linear polyesters are obtained with a wide range of properties and uses. Predominant in terms of volume and product value are those based on poly(ethylene terephthalate) (PET). Aliphatic polyesters of technical importance are typified by the poly(alkylene adipate)s and by poly(ϵ -caprolactone). In particular, their dihydroxy-terminated oligomeric polyesters with molecular weight up to 5000 are used for the production of polyurethanes¹¹. Typical diols used in the adipate synthesis include in this case ethylene glycol, diethylene glycol, 1,4-butanediol and 1,6-hexanediol. Increasing the length of the alkylene chain decreases the concentration of ester groups, resulting in

reduced polarity, increased hydrolytic stability, and increased flexibility. Succinates and adipates find also applications as non-migrating plasticizers for PVC¹², while polylactic acid (PLA)¹³⁻¹⁵, polyglycolic acid (PGA) and their copolymers (PLGA)¹⁶⁻¹⁸ form the basis for biosorbable surgical sutures as well as drug delivery devices, prosthetic and bone screw devices and plates for temporary internal fracture fixation¹⁹.

As far as the current market for linear aliphatic and biodegradable polyesters is concerned, a series of biodegradable aliphatic polyesters, trademarked 'BIONOLLE', such as polybutylene succinate, poly(butylene succinate-adipate) copolymer and polyethylene succinate with high molecular weights ranging from several tens of thousands to several hundreds of thousands were invented in 1990 and produced successfully through polycondensation reaction of glycols with aliphatic dicarboxylic acids and others²⁰. A pilot plant with a capacity of 10 tons/year was built in 1991, and a semi-commercial plant with a capacity of 3000 tons/year was constructed in 1993. BIONOLLE is a white crystalline thermoplastic, has melting points ranging about 90 to 120 °C, glass transition temperatures ranging about -45 to -10 °C and density about 1.25 g/cm³. BIONOLLE has excellent processability, so it can be processed on conventional equipment (commonly used in processing polyolefins) at temperature of 160 to 200 °C into various molded products such as injected, extruded and blown ones. A new grade of BIONOLLE, which has a long chain branch (LCB), high melt tension and high recrystallization rate, has been recently developed, to enable stretched blown bottles and highly expanded foams to be made easily.